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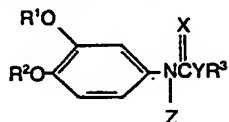
(71) Applicant: **SUMITOMO CHEMICAL COMPANY, LIMITED,**
15 Kitahama 5-chome Higashi-ku, Osaka-shi Osaka-fu
(JP)

(72) Inventor: **Noguchi, Hiroshi, 10-3-318,**
Sonehigashi-machi, 2-chome, Toyonaka Osaka (JP)
Inventor: **Kato, Toshiro, 8-D-410, Sakasada, 1-chome,**
Takarazuka Hyogo (JP)
Inventor: **Takahashi, Junya, 4-2-303, Ryodo-cho,**
Nishinomiya Hyogo (JP)
Inventor: **Ishiguri, Yukio, 14-7, Mefu, 2-chome,**
Takarazuka Hyogo (JP)
Inventor: **Yamamoto, Shigeo, 2-16, Koda 2-chome, Ikeda**
Osaka (JP)
Inventor: **Kamoshita, Katsuzo, 3-11 Kofudal, 2-chome**
Toyono-cho, Toyono-gun Osaka (JP)

(74) Representative: **Allard, Susan Joyce et al, BOULT,**
WADE & TENNANT 27 Farnival street, London EC4A 1PQ
(GB)

(54) **Fungicidal N-phenylcarbamates.**

(57) The use of an N-phenylcarbamate of the formula:



as a fungicidal agent against phytopathogenic fungi, particularly those strains which are resistant to benzimidazole thiophanate fungicides and/or cyclic imide fungicides.

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FUNGICIDAL N-PHENYLCARBAMATES

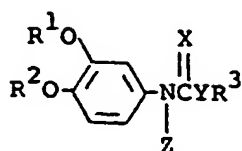
This invention relates to fungicidal N-phenyl-carbamates.

5 Benzimidazole thiophanate fungicides such as Benomyl (methyl 1-(butylcarbamoyl)benzimidazol-2-ylcarbamate), Fubelidazol (2-(2-furyl)benzimidazole), Thiabendazole (2-(4-thiazolyl)benzimidazole), Carbendazim (methyl benzimidazol-2-ylcarbamate), Thiophanate-methyl (1,2-bis(3-
10 methoxycarbonyl-2-thioureido)benzene), Thiophanate (1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene), 2-(O,S-dimethylphosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene and 2-(O,O-dimethylthiophosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene are known to show an ex-
15 cellent fungicidal activity against various plant pathogenic fungi, and they have been widely used as agricultural fungicides since 1970. However, their continuous application over a long period of time provides phytopathogenic fungi with tolerance to them, whereby their plant disease-
20 preventive effect is lowered. Further, the fungi which have gained tolerance to certain kinds of benzimidazole thiophanate fungicides also show considerable tolerance to some other kinds of benzimidazole thiophanate fungicides. Thus, they are apt to acquire a cross tolerance. Therefore if any
25 significant decrease of their plant disease-preventive effect in certain fields is observed, their application in such fields has to be discontinued. However, it is often observed

that the density of drug-resistant organisms does not decrease even long after the discontinuation of the use. Although other kinds of fungicides have to be employed in these cases, only a few are as effective as benzimidazole thiophanate fungicides in controlling various phytopathogenic fungi. Cyclic imide fungicides such as Procymidone (3-(3',5'-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide), Iprodione (3-(3',5'-dichlorophenyl)-1-isopropylcarbamoyleimidazolidine-2,4-dione),
10 Vinchlozoline (3-(3',5'-(dichlorophenyl)-5-methyl-5-vinyl-oxazolidin-2,4-dione), ethyl (RS)-3-(3',5'-dichlorophenyl)-5-methyl-2,4-dioxooxazolidine-5-carboxylate, etc., which are effective against various plant diseases, particularly those caused by Botrytis cinerea, have the same defects as previously explained with respect to the benzimidazole thio-
15 phanate fungicides.

In C.R. Acad. Sc. Paris, t. 289, S'erie D, pages 691-693 (1979), it is described that such herbicides as Barban (4-chloro-2-butynyl N-(3-chlorophenyl)carbamate),
20 Chlcrobufam (1-methyl-2-propynyl N-(3-chlorophenyl)carbamate), Chlorpropham (isopropyl N-(3-chlorophenyl)carbamate) and Propham (isopropyl N-phenylcarbamate) exhibit a fungicidal activity against certain organisms which show a tolerance to some benzimidazole thiophanate fungicides. However,
25 their fungicidal activity against drug-resistant fungi is not very strong, and hence in practice they can not be used as fungicides.

We have now found that N-phenylcarbamates of the formula :



(I) .

wherein R^1 and R^2 are the same or different and each represent a lower alkyl group, a lower alkenyl group, a lower alkynyl group or a lower alkyl group substituted with at least one halogen atom, lower alkoxy or lower cycloalkyl group; R^3 is a C_1 - C_8 alkyl group, a C_3 - C_8 alkenyl group, a C_3 - C_8 alkynyl group, lower cycloalkyl group, a lower haloalkenyl group, a lower haloalkynyl group, a lower aralkyl group, a lower alkyl group substituted with at least one halogen atom, cyano, lower alkoxy, lower alkenyloxy, lower haloalkoxy, phenoxy, lower aralkyloxy or lower cycloalkyl group,

or a group of the formula: $\begin{array}{c} (\text{CH}_2)_m \\ \diagup \quad \diagdown \\ -\text{CH} \quad \text{O} \\ \diagdown \quad \diagup \\ (\text{CH}_2)_n \end{array}$ in which m is 0, 1

or 2, n is 1, 2 or 3; X and Y are the same or different and each represent an oxygen atom or a sulfur atom; and Z is a hydrogen atom, a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a lower cycloalkyl group, a lower haloalkenyl group, a lower alkyl group substituted with at least one halogen atom, cyano, lower alkoxy or lower alkoxycarbonyl group, or a group of the formula:

-COR⁴ or -SO₂R⁴ in which R⁴ is a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a lower cycloalkyl group, a lower haloalkenyl group, a lower alkyl group substituted with at least one halogen atom, cyano, lower alkoxy, lower cycloalkyl or phenoxy group (the phenoxy group optionally being substituted with at least one halogen atom and/or at least one alkyl group), a phenyl group, a furyl group, a thienyl group, a phenyl group substituted with at least one halogen atom, cyano, nitro, trifluoromethyl, lower alkyl or lower alkoxy group, or an aralkyl group (the aralkyl group optionally being substituted with at least one halogen atom and/or at least one alkyl group), with the proviso that when R¹ is methyl, R² is not methyl or butyl, show an excellent fungicidal activity against plant pathogenic fungi which have developed resistance to benzimidazole thiophanate fungicides and/or cyclic imide fungicides. It is notable that their fungicidal potency against the organisms tolerant to benzimidazole thiophanate fungicides and/or cyclic imide fungicides (hereinafter referred to as "drug-resistant fungi" or "drug-resistant strains") is much higher than that against organisms sensitive to benzimidazole thiophanate fungicides and/or cyclic fungicides (hereinafter referred to as "drug-sensitive fungi" or "drug-sensitive strains").

By the term "lower" used herein in connection with organic radicals or compounds is meant that such radicals or compounds each have not more than 6

carbon atoms.

Some N-(3,4-dialkoxyphenyl)carbamates have previously been synthesized, for example, N-(3,4-dimethoxyphenyl)carbamates (C.A., 28, 2339; 50, 5674e), 2-chloroethyl N-(3-methoxy-4-octyloxyphenyl)carbamate (C.A., 55, 13376f; 55, 21021b), 2-chloroethyl N-(3-methoxy-4-butoxyphenyl)carbamate (C.A., 64, 8063g), and ethyl N-(3-methoxy-4-octyloxyphenyl)carbamate (C.A., 68, 39300b) are known. However, none of them shows any substantial fungicidal activity against drug-resistant fungi nor is useful as a fungicide.

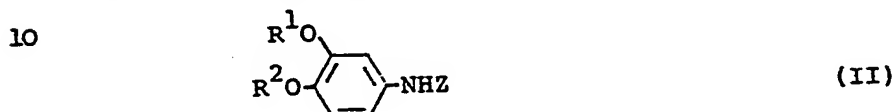
Thus, the present invention provides a fungicidal composition which comprises, as an active ingredient, a fungicidally effective amount of the N-phenylcarbamate (I) together with an inert carrier or diluent. It also provides a combination composition comprising as active ingredients the N-phenylcarbamate (I) together with a benzimidazole thiophanate fungicide and/or a cyclic imide fungicide, which is fungicidally effective against not only drug-sensitive fungi but also drug-resistant fungi, and hence particularly effective for the prevention of plant diseases. It also provides a method of controlling plant pathogenic fungi including drug-resistant strains and drug-sensitive strains by applying a fungicidally effective amount of the N-phenylcarbamate (I) to plant pathogenic fungi. It further provides novel N-phenylcarbamates which are represented by the formula (I) wherein R^1 , R^2 , R^3 , X, Y and Z are each as

defined above with the proviso that when R^1 is methyl, R^2 is not methyl or butyl. It furthermore provides a process for producing the novel N-phenylcarbamates (I).

The N-phenylcarbamates (I) can be prepared by various procedures, typical examples of which are given below:

Procedure (a):-

The N-phenylcarbamate (I) is obtained by reacting a 3,4-dialkoxyaniline of the formula:



wherein R^1 , R^2 and Z are each as defined above, with a chloroformate of the formula:



wherein R^3 , X and Y are each as defined above.

The reaction is usually carried out in the presence of an inert solvent (e.g. benzene, toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, chloroform, carbon tetrachloride, ethyl acetate, pyridine, dimethylformamide). When desired, the reaction may be performed in the presence of a dehydrohalogenating agent (e.g. pyridine, triethylamine, diethylaniline, sodium hydroxide, potassium hydroxide, sodium hydride) to obtain the desired compound (I) in a high yield. The reaction may be carried out at a temperature in the range of from 0 to 150°C instantaneously or within 12

20

25


Procedure (b) :-

$$\begin{array}{c} \text{R}^1\text{O} \\ | \\ \text{C}_6\text{H}_3 \\ | \\ \text{R}^2\text{O} \end{array} \text{NC=X} \quad (\text{IV})$$
$$\text{HYR}^3 \quad (V)$$

The reaction may be carried out in the absence of a solvent or in the presence of an inert solvent (e.g. benzene, toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, dimethylformamide, chloroform, carbon tetrachloride). If desired, a catalyst (e.g. triethylamine, diethylaniline, 1,4-diazabicyclo(2,2,2)octane) may be used. The reaction is normally carried out at a temperature in the range of from 0 to 50°C instantaneously or within 12 hours.

Procedure (c) :-

25



(VI)

wherein R^1 , R^2 , R^3 , X and Y are each as defined above, with a halide of the formula:

A-Z

(VII)

wherein Z is as defined above but is other than hydrogen
5 and A is a halogen atom (e.g. chlorine, bromine).

The reaction is usually carried out in an inert solvent (e.g. benzene, toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, chloroform, carbon tetrachloride, ethyl acetate, pyridine, dimethylformamide). If desired,
10 the reaction may be carried out in the presence of a dehydrohalogenating agent (e.g. pyridine, triethylamine, diethylaniline, sodium hydroxide, potassium hydroxide, sodium hydride) and a catalyst (e.g. tetrabutylammonium bromide) to obtain the desired compound (I) in a high
15 yield. The reaction may be carried out at a temperature in the range of from 0 to 150°C instantaneously or within 12 hours.

As specific examples of the symbols used in the above formula, R^1 and R^2 are each preferably methyl, ethyl, n-propyl, isopropyl, n-butyl, allyl, 2-butenyl, 3-butenyl, propargyl, 3-butyne, difluoromethyl, 2-chloroethyl, 2,2,2-trifluoroethyl, 2-methoxyethyl or cyclopropylmethyl, R^3 is methyl, ethyl, n-propyl, isopropyl, sec-butyl, 1-ethylpropyl, 1-methylbutyl, 1-ethylbutyl, 1,3-dimethylbutyl, 1-methylheptyl, allyl, 1-methyl-2-propenyl, 2-butenyl, 3-butenyl, 2-methyl-2-propenyl, 1-ethyl-2-propenyl, 1-methyl-3-butenyl, 1-pentyl-2-propenyl, propargyl, 1-methyl-2-propynyl, 2-butyne, 3-butyne, 1-ethyl-2-propynyl,

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1-methyl-3-butynyl, 1-butyl-2-propynyl, 1-pentyl-2-propynyl, cyclobutyl, cyclopentyl, 2-fluoroethyl, 2-chloroethyl, 2,2-dichloroethyl, 1-methyl-2-bromoethyl, 1-fluoromethyl-2-fluoroethyl, 1-bromomethyl-2-bromoethyl, 1-methyl-2,2,2-tri-
 5 chloroethyl, 1-ethyl-2-bromoethyl, 4-chloro-2-butenyl, 4-chloro-2-butynyl, 2-cyanoethyl, 1-methyl-2-methoxyethyl, 1-methyl-2-butoxyethyl, 2-allyloxyethyl, 2-(2-chloroethoxy)-ethyl, 2-benzyloxyethyl, 1-chloroethyl-2-methoxyethyl, cyclopropylmethyl, 1-cyclopropylethyl, 1-cyclopentylethyl,
 10 3-furylmethyl, 1-phenylethyl or 3-tetrahydrofuryl, X and Y are each oxygen or sulfur, and Z is hydrogen, methyl, ethyl, n-butyl, allyl, acetyl, propionyl, n-butanoyl, sec-butanoyl, cyclopropanecarbonyl, benzoyl, 2-chlorobenzoyl, 2,4-di-chlorobenzoyl, 4-methylbenzoyl, methanesulfonyl or ethoxy-
 15 carbonylmethyl.

The N-phenylcarbarnates (I) are fungicidally effective against a wide variety of plant pathogenic fungi, of which examples are as follows: Podosphaera leucotricha, Venturia inaequalis, Mycosphaerella pomi, Marssonina mali
 20 and Sclerotinia mali of apple, Phyllactinia kakicola and Gloeosporium kaki of persimmon, Cladosporium carpophilum and Phomopsis sp. of peach, Cercospora viticola, Uncinula necator, Elsinoe ampelina and Glomerella cingulata of grape, Cercospora beticola of sugarbeet, Cercospora arachidicola
 25 and Cercospora personata of peanut, Erysiphe graminis f. sp. hordei, Cercospora herpotrichoides and Fusarium nivale of barley, Erysiphe graminis f. sp. tritici of wheat,

Sphaerotheca fuliginea and Cladosporium cucumerinum of cucumber, Cladosporium fulvum of tomato, Corynespora melongenae of eggplant, Sphaerotheca humuli, Fusarium oxysporum f. sp. fragariae of strawberry, Botrytis alli of onion, Cercospora apii of celery, Phaeoisariopsis griseola of kidney bean, Erysiphe cichoracearum of tobacco, Diplocarpon rosae of rose, Elsinoe fawcetti, Penicillium italicum, Penicillium digitatum of orange, Botrytis cinerea of cucumber, eggplant, tomato, strawberry, pimiento, onion, lettuce, grape, orange, cyclamen, rose or hop, Sclerotinia sclerotiorum of cucumber, eggplant, pimiento, lettuce, celery, kidney bean, soybean, azuki bean, potato or sunflower, Sclerotinia cinerea of peach or cherry, Mycosphaerella melonis of cucumber or melon, etc. Thus the N-phenylcarbamates (I) are highly effective in controlling the drug-resistant strains of the fungi.

The N-phenylcarbamates (I) are also fungicidally effective against fungi sensitive to known fungicides as well as fungi against which known fungicides are ineffective. Examples of such fungi are Pyricularia oryzae, Pseudoperonospora cubensis, Plasmopara viticola, Phytophthora infestans, etc.

Advantageously, the N-phenylcarbamates (I) possess a low toxicity and do not have a detrimental effect on mammals, fishes etc. Also, they may be applied to agricultural fields without causing any significant toxicity to important crop plants.

In view of their excellent fungicidal properties, the preferred compounds of formula (I) are those wherein R^1 and R^2 are independently methyl, ethyl, n-propyl, isopropyl, n-butyl, allyl, 2-butenyl, 3-butenyl, propargyl, 3-butyne, difluoromethyl, 2-chloroethyl, 2,2,2-trifluoroethyl, 2-methoxyethyl or cyclopropylmethyl, R^3 is methyl, ethyl, n-propyl, isopropyl, sec-butyl, 1-ethylpropyl, 1-methylbutyl, 1-ethylbutyl, 1,3-dimethylbutyl, 1-methylheptyl, allyl, 1-methyl-2-propenyl, 2-butenyl, 3-butenyl, 2-methyl-2-propenyl, 1-ethyl-2-propenyl, 1-methyl-3-butenyl, 1-pentyl-2-propenyl, propargyl, 1-methyl-2-propynyl, 2-butyne, 3-butyne, 1-ethyl-2-propynyl, 1-methyl-3-butyne, 1-butyl-2-propynyl, 1-pentyl-2-propynyl, cyclobutyl, cyclopentyl, 2-fluoroethyl, 2-chloroethyl, 2,2-dichloroethyl, 1-methyl-2-bromoethyl, 1-fluoromethyl-2-fluoroethyl, 1-bromoethyl-2-bromoethyl, 1-methyl-2,2,2-trichloroethyl, 1-ethyl-2-bromoethyl, 4-chloro-2-butenyl, 4-chloro-2-butyne, 2-cyanoethyl, 1-methyl-2-methoxyethyl, 1-methyl-2-butoxyethyl, 2-allyloxyethyl, 2-(2-chloroethoxy)ethyl, 2-benzyloxyethyl, 1-chloroethyl-2-methoxyethyl, cyclopropylmethyl, 1-cyclopropylethyl, 1-cyclopentylethyl, 2-furylmethyl, 1-phenylethyl or 3-tetrahydrofuryl, X and Y are independently oxygen or sulfur, and Z is hydrogen, methyl, ethyl, n-butyl, allyl, acetyl, propionyl, n-butanoyl, sec-butanoyl, cyclopropanecarbonyl, benzoyl, 2-chlorobenzoyl, 2,4-dichlorobenzoyl, 4-methylbenzoyl, methanesulfonyl or ethoxycarbonylmethyl, with the proviso that when R^1 is methyl, R^2 is

not methyl or butyl.

Particularly preferred are the compounds of formula (I) wherein R^1 and R^2 are independently methyl, ethyl, n-propyl, allyl or propargyl, R^3 is ethyl, isopropyl, sec-butyl, 1-methylbutyl, 1-ethylpropyl, 1-ethylbutyl, 1-methyl-2-propenyl, 1-ethyl-2-propenyl, 1-methyl-3-butenyl, propargyl, 1-methyl-2-propynyl, 1-ethyl-2-propynyl, 3-butynyl, 1-methyl-3-butynyl, 1-butyl-2-propynyl, 2-fluoroethyl, 1-methyl-2-bromoethyl, 1-fluoromethyl-2-fluoroethyl, 1-bromomethyl-2-bromoethyl, 4-chloro-2-butynyl, 1-methyl-2-methoxyethyl, 1-cyclopropylethyl or 1-phenylethyl, X is oxygen, Y is oxygen or sulfur, and Z is hydrogen, acetyl, propionyl, n-butanoyl, sec-butanoyl, cyclopropanecarbonyl, benzoyl, 2-chlorobenzoyl, 2,4-dichlorobenzoyl or 4-methylbenzoyl, with the proviso that when R^1 is methyl, R^2 is not methyl.

More preferred are the compound of formula (I) wherein R^1 and R^2 are each ethyl, R^3 is ethyl, isopropyl, sec-butyl, 1-methylbutyl, 1-ethylbutyl, 1-ethyl-3-butenyl, 1-methyl-2-propynyl, 4-chloro-2-butynyl or 1-phenylethyl, X is oxygen, Y is oxygen or sulfur and Z is hydrogen, acetyl, cyclopropanecarbonyl, benzoyl or 2-chlorobenzoyl.

Most preferred are the following :

- Isopropyl N-(3,4-diethoxyphenyl)carbamate;
- 1-Methyl-2-propynyl N-(3,4-diethoxyphenyl)-carbamate;
- 4-Chloro-2-butynyl N-(3,4-diethoxyphenyl)-

carbamate;

Isopropyl N-(3,4-diethoxyphenyl)thiolcarbamate;

1-Phenylethyl N-(3,4-diethoxyphenyl)carbamate;

Isopropyl N-acetyl-N-(3,4-diethoxyphenyl)carba-
5 mate;

Isopropyl N-cyclopropanecarbonyl-N-(3,4-diethoxy-
phenyl)carbamate;

Isopropyl N-benzoyl-N-(3,4-diethoxyphenyl)carba-
mate;

10 Isopropyl N-(2-chlorobenzoyl)-N-(3,4-diethoxy-
phenyl)carbamate.

The processes for preparation of the N-phenyl-
carbamates (I) are illustrated in the following examples

15 Example 1

Preparation of isopropyl N-(3,4-diethoxyphenyl)-
carbamate according to Procedure (a):-

3,4-Diethoxyaniline (1.8 g) and diethylaniline
(1.5 g) were dissolved in benzene (20 ml). To the resultant
20 solution was dropwise added isopropyl chloroformate (1.2 g)
in 5 minutes under ice-cooling. After being allowed to
stand at room temperature for 3 hours, the reaction mixture
was poured into ice-water and extracted with ether. The
extract was washed with water, dried over magnesium sulfate
25 and concentrated under reduced pressure to give crude
crystals (2.6 g). Recrystallization from ethanol gave
isopropyl N-(3,4-diethoxyphenyl)carbamate (Compound No. 13)

(2.3 g) in a yield of 86 %. M.P., 100 - 100.5°C.

Elementary analysis: Calcd. for $C_{14}H_{21}NO_4$: C, 62.90 %; H, 7.92 %; N, 5.24 %. Found: C, 62.75 %; H, 7.96 %; N, 5.41 %.

5 Example 2

Preparation of isopropyl N-(3,4-diethoxyphenyl)-thiolcarbamate according to Procedure (b):-

Triethylamine (1 g) and isopropyl mercaptan (0.8 g) were dissolved in toluene (20 ml). To the resultant
10 solution was dropwise added 3,4-diethoxyphenyl isocyanate (2.1 g) in 5 minutes under ice-cooling. After allowed to stand at room temperature for 12 hours, the reaction mixture was poured into ice-water and extracted with toluene. The extract was washed with water, dried over magnesium sulfate
15 and concentrated under reduced pressure. The residue was purified by silica gel chromatography using toluene as the eluent to give isopropyl N-(3,4-diethoxyphenyl)thiolcarbamate (Compound No. 88) (2.7 g) in a yield of 95 %. M.P., 110 - 111°C.

20 Elementary analysis: Calcd. for $C_{14}H_{21}NO_3S$: C, 59.33 %; H, 7.47 %; N, 4.94 %; S, 11.32 %. Found: C, 59.02 %; H, 7.51 %; N, 4.89 %; S, 11.70 %.

Example 3

Preparation of isopropyl N-benzoyl-N-(3,4-di-
25 ethoxyphenyl)carbamate according to Procedure (c):-

Isopropyl N-(3,4-diethoxyphenyl)carbamate (2.7 g) was dissolved in dimethylformamide (50 ml), and sodium

hydride dispersion (50 %, 0.5 g) was added thereto. The mixture was heated at 60°C for 15 minutes, treated with benzoyl chloride (1.4 g) and heated for 30 minutes. The reaction mixture was poured into ice-water and extracted with ether. The extract was washed with sodium bicarbonate solution and saturated brine, dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography using hexane-acetone as the eluent to give isopropyl N-benzoyl-N-(3,4-diethoxyphenyl)carbamate (Compound No. 99) (3.1 g) in a yield of 80 %. M.P., 120 - 121°C.

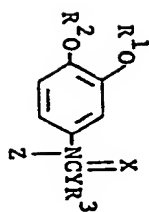
Elementary analysis: Calcd. for $C_{21}H_{25}NO_5$: C, 67.90 %; H, 6.78 %; N, 3.77 %. Found: C, 68.11 %; H, 6.61 %; N, 3.90 %.

According to either one of the above Procedures (a), (b) or (c), the N-phenylcarbamates of the formula (I) as shown in Table 1 can be prepared:

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Table 1



Compound No.	R ¹	R ²	R ³	X	Y	Z	Physical constant
1	-CH ₃	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	H	M.P. 104-105°C
2	-CH ₃	-C ₂ H ₅	C≡CH -CHCH ₃	0	0	H	M.P. 133-134°C
3	-CH ₃	-C ₂ H ₅	CH ₃ -CHCH ₂ OCH ₃	0	0	H	M.P. 54-55°C
4	-CH ₃	-C ₃ H ₇ (n)	-C ₃ H ₇ (iso)	0	0	H	M.P. 94-95°C
5	-CH ₃	-CH ₂ CH=CH ₂	-C ₃ H ₇ (iso)	0	0	H	M.P. 79-80°C
6	-CH ₃	-CH ₂ CH=CH ₂	C≡CH -CHCH ₃	0	0	H	M.P. 106-107°C
7	-CH ₃	-CH ₂ C≡CH	-C ₃ H ₇ (iso)	0	0	H	¹⁹ n _D 1.5269
8	-C ₂ H ₅	-CH ₃	-C ₃ H ₇ (iso)	0	0	H	M.P. 103-104°C
9	-C ₂ H ₅	-CH ₃	C≡CH -CHCH ₂ CH ₃	0	0	H	M.P. 110.5-111.5°C

(Continued)

Compound No.	R ¹	R ²	R ³	X	Y	Z	Physical constant
10	-C ₂ H ₅	-CH ₃	-CH ₂ C≡CH ₂ Cl	0	0	H	M.P. 96-97°C
11	-C ₂ H ₅	-C ₂ H ₅	-CH ₃	0	0	H	M.P. 120-121°C
12	-C ₂ H ₅	-C ₂ H ₅	-C ₂ H ₅	0	0	H	M.P. 90-91°C
13	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	H	M.P. 100-100.5°C
14	-C ₂ H ₅	-C ₂ H ₅	-C ₄ H ₉ (sec)	0	0	H	M.P. 97-98°C
15	-C ₂ H ₅	-C ₂ H ₅	CH ₃ -CH(CH ₂) ₂ CH ₃	0	0	H	M.P. 67-68°C
16	-C ₂ H ₅	-C ₂ H ₅	CH ₂ CH ₃ -CHCH ₂ CH ₃	0	0	H	M.P. 93-94°C
17	-C ₂ H ₅	-C ₂ H ₅	CH ₂ CH ₃ -CH(CH ₂) ₂ CH ₃	0	0	H	M.P. 87-88°C
18	-C ₂ H ₅	-C ₂ H ₅	CH ₃ CH ₃ -CHCH ₂ CHCH ₃	0	0	H	M.P. 56-57°C
19	-C ₂ H ₅	-C ₂ H ₅	CH ₃ -CH(CH ₂) ₅ CH ₃	0	0	H	M.P. 46.5-48°C
20	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ CH=CH ₂	0	0	H	M.P. 86-87°C


(Continued)

Compound No.	R ¹	R ²	R ³	X	Y	Z	Physical constant
21	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CHCH}=\text{CH}_2 \end{array}$	0	0	H	M.P. 98-99.5°C
22	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ CH ₂ CH=CH ₂	0	0	H	M.P. 92.5-93.5°C
23	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2\text{C}=\text{CH}_2 \end{array}$	0	0	H	M.P. 92-93°C
24	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ -\text{CHCH}=\text{CH}_2 \end{array}$	0	0	H	M.P. 98.5-99.5°C
25	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CHCH}_2\text{CH}=\text{CH}_2 \end{array}$	0	0	H	M.P. 75-76°C
26	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{CH}=\text{CH}_2 \\ \\ -\text{CH}(\text{CH}_2)_4\text{CH}_3 \end{array}$	0	0	H	M.P. 46.5-48°C
27	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ C=CH	0	0	H	M.P. 111-112°C
28	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CHC}\equiv\text{CH} \end{array}$	0	0	H	M.P. 116-117°C
29	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ CH ₂ C≡CH	0	0	H	M.P. 89-90°C

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(Continued)

Compound No.	R ¹	R ²	R ³	X	Y	Z	Physical constant
30	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ -\text{CHC}\equiv\text{CH} \end{array}$	0	0	H	M.P. 118-119°C
31	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CHCH}_2\text{C}\equiv\text{CH} \end{array}$	0	0	H	M.P. 99-100°C
32	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{C}\equiv\text{CH} \\ \\ -\text{CH}(\text{CH}_2)_3\text{CH}_3 \end{array}$	0	0	H	M.P. 120-121°C
33	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{C}\equiv\text{CH} \\ \\ -\text{CH}(\text{CH}_2)_4\text{CH}_3 \end{array}$	0	0	H	M.P. 96-97°C
34	-C ₂ H ₅	-C ₂ H ₅		0	0	H	M.P. 114-115.5°C
35	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ CH ₂ F	0	0	H	M.P. 101-102°C
36	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ CH ₂ Cl	0	0	H	M.P. 89.5-90.5°C
37	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ CHCl ₂	0	0	H	M.P. 73-74°C
38	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CHCH}_2\text{Br} \end{array}$	0	0	H	M.P. 69-70°C

(Continued)

Compound No.	R ¹	R ²	R ³	X	Y	Z	Physical constant
39	-C ₂ H ₅	-C ₂ H ₅	CH ₂ F -CHCH ₂ F	0	0	H	M.P. 89-90°C
40	-C ₂ H ₅	-C ₂ H ₅	CH ₂ Br -CHCH ₂ Br	0	0	H	M.P. 75-76°C
41	-C ₂ H ₅	-C ₂ H ₅	CH ₃ -CHOC ₂ H ₅	0	0	H	^{19.5} n _D 1.5316
42	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ CH=CHCH ₂ Cl	0	0	H	M.P. 82-83°C
43	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ C≡CHCH ₂ Cl	0	0	H	M.P. 112-113°C
44	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ CH ₂ OCH ₂ CH=CH ₂	0	0	H	M.P. 58-59°C
45	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ CH ₂ OCH ₂ CH ₂ Cl	0	0	H	M.P. 77-78°C
46	-C ₂ H ₅	-C ₂ H ₅	CH ₃ -CHCH ₂ OCH ₃	0	0	H	M.P. 65-66.5°C
47	-C ₂ H ₅	-C ₂ H ₅	CH ₃ -CHCH ₂ O(CH ₂) ₃ CH ₃	0	0	H	M.P. 36-38°C
48	-C ₂ H ₅	-C ₂ H ₅	CH ₂ Cl -CHCH ₂ OCH ₃	0	0	H	M.P. 82-83°C



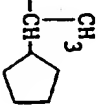
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Compound No.	R ¹	R ²	R ³	X	Y	Z	Physical constant
49	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ CH ₂ CN	0	0	H	M.P. 85.5-86.5°C
50	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}-\triangle \end{array}$	0	0	H	M.P. 107-108°C
51	-C ₂ H ₅	-C ₃ H ₇ (n)	-C ₂ H ₅	0	0	H	M.P. 74-75°C
52	-C ₂ H ₅	-C ₃ H ₇ (n)	-C ₃ H ₇ (iso)	0	0	H	M.P. 97-98°C
53	-C ₂ H ₅	-C ₂ H ₅	$\begin{array}{c} \text{C}\equiv\text{CH} \\ \\ -\text{CHCH}_3 \end{array}$	0	0	H	M.P. 99-100°C
54	-C ₂ H ₅	-C ₄ H ₉ (n)	-C ₃ H ₇ (iso)	0	0	H	M.P. 110-111°C
55	-C ₂ H ₅	-C ₄ H ₉ (n)	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CHCH}_2\text{OCH}_3 \end{array}$	0	0	H	M.P. 87-88°C
56	-C ₂ H ₅	-CH ₂ C≡CH	-C ₃ H ₇ (iso)	0	0	H	M.P. 102-103°C
57	-C ₃ H ₇ (n)	-CH ₃	-C ₃ H ₇ (iso)	0	0	H	M.P. 101-102°C
58	-C ₃ H ₇ (n)	-C ₂ H ₅	-CH ₃	0	0	H	M.P. 85-86°C
59	-C ₃ H ₇ (n)	-C ₂ H ₅	-C ₂ H ₅	0	0	H	M.P. 76.5-77.5°C
60	-C ₃ H ₇ (n)	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	H	M.P. 81-82°C




(Continued)

Compound No.	R ¹	R ²	R ³	X	Y	Z	Physical constant
61	-C ₃ H ₇ (n)	-C ₂ H ₅	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CHCH}_2\text{CH}_2 \end{array}$	0	0	H	M.P. 83-84°C
62	-C ₃ H ₇ (n)	-C ₂ H ₅	$\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ -\text{CHCH}_2\text{CH}_3 \end{array}$	0	0	H	M.P. 90-91°C
63	-C ₃ H ₇ (n)	-C ₂ H ₅	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}-\triangle \end{array}$	0	0	H	M.P. 82-83°C
64	-C ₃ H ₇ (n)	-C ₂ H ₅	-CH ₂ CH ₂ F	0	0	H	M.P. 82-83°C
65	-C ₃ H ₇ (n)	-C ₃ H ₇ (n)	-C ₃ H ₇ (iso)	0	0	H	M.P. 85-86°C
66	-C ₃ H ₇ (iso)	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	H	η_D^{19} 1.5121
67	-C ₃ H ₇ (iso)	-C ₂ H ₅	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CHC}\equiv\text{CH} \end{array}$	0	0	H	M.P. 100.5-102°C
68	-C ₃ H ₇ (iso)	-C ₂ H ₅	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CHCH}_2\text{OCH}_3 \end{array}$	0	0	H	η_D^{19} 1.5092
69	-C ₄ H ₉ (n)	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	H	M.P. 79.5-81°C
70	-CH ₂ CH=CH ₂	-C ₃ H ₇ (n)	-C ₃ H ₇ (iso)	0	0	H	M.P. 82-83°C



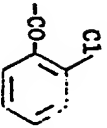
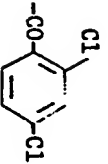

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Compound No.	R ¹	R ²	R ³	X	Y	Z	Physical constant
71	$-\text{CH}_2\text{CH}=\text{CH}_2$	$-\text{C}_3\text{H}_7(\text{n})$	$-\text{CH}_2\text{CH}=\text{CHCH}_3$	0	0	H	M.P. 66-67°C
72	$-\text{CH}_2\text{CH}=\text{CH}_2$	$-\text{C}_3\text{H}_7(\text{n})$	$-\text{CH}_2\text{C}=\text{CCH}_3$	0	0	H	M.P. 92-93°C
73	$-\text{CH}_2\text{CH}=\text{CH}_2$	$-\text{C}_3\text{H}_7(\text{n})$	$\text{C}\equiv\text{CH}$	0	0	H	M.P. 84-85.5°C
			$-\text{CHCH}_3$				
74	$-\text{CH}_2\text{CH}=\text{CH}_2$	$-\text{CH}_2\text{CH}=\text{CH}_2$	$-\text{C}_3\text{H}_7(\text{iso})$	0	0	H	M.P. 83.5-84.5°C
75	$-\text{CH}_2\text{C}=\text{CH}_2$	$-\text{C}_2\text{H}_5$	$-\text{C}_3\text{H}_7(\text{iso})$	0	0	H	M.P. 101-102°C
76	$-\text{CH}_2\text{C}=\text{CH}_2$	$-\text{CH}_2\text{C}\equiv\text{CH}$	$-\text{C}_3\text{H}_7(\text{iso})$	0	0	H	M.P. 103-104°C
77	$-\text{CHF}_2$	$-\text{CHF}_2$	$-\text{C}_3\text{H}_7(\text{iso})$	0	0	H	n_D^{22} 1.4671
78	$-\text{C}_2\text{H}_5$	$-\text{C}_2\text{H}_5$	$-\text{CH}_2\text{CH}_2\text{OCH}_2$ 	0	0	H	M.P. 73-74°C
79	$-\text{C}_2\text{H}_5$	$-\text{C}_2\text{H}_5$	$-\text{CH}_2$ 	0	0	H	M.P. 95-96°C
80	$-\text{C}_2\text{H}_5$	$-\text{C}_2\text{H}_5$	CH_3 	0	0	H	M.P. 105-106°C
81	$-\text{C}_2\text{H}_5$	$-\text{C}_2\text{H}_5$	CH_2CH_3 $-\text{CHCH}_2\text{Br}$	0	0	H	M.P. 68-69°C

(Continued)

Compound No.	R ¹	R ²	R ³	X	Y	Z	Physical constant
82	-CH ₂ CH ₂ Cl	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	H	M.P. 111-112°C
83	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (n)	0	0	H	M.P. 79-80°C
84	-C ₂ H ₅	-C ₂ H ₅		0	0	H	M.P. 117-118°C
85	-C ₂ H ₅	-C ₂ H ₅		0	0	H	M.P. 111.5-112.5°C
86	-C ₂ H ₅	-C ₂ H ₅		0	0	H	M.P. 109-110°C
87	-C ₂ H ₅	-C ₂ H ₅	-C ₂ H ₅	0	S	H	M.P. 107-108°C
88	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	S	H	M.P. 110-111°C
89	-C ₂ H ₅	-C ₂ H ₅	-CH ₂ CH=CH ₂	0	S	H	M.P. 73-76°C
90	-C ₂ H ₅	-C ₂ H ₅	-C ₂ H ₅	0	0	-CH ₃	28.5 1.5059 n _D
91	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	-C ₂ H ₅	28.5 1.4922 n _D
92	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	-C ₄ H ₉ (n)	26.5 1.4885 n _D
93	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	-CH ₂ CH=CH ₂	26.5 1.5044 n _D

(Continued)

Compound No.	R ¹	R ²	R ³	X	Y	Z	Physical constant
94	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	-COCH ₃	M.P. 98-99°C
95	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	-COC ₂ H ₅	$n_D^{27.5}$ 1.5006
96	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	-COC ₄ H ₉ (n)	M.P. 63-65°C
97	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	-COC ₄ H ₉ (sec)	n_D^{28} 1.4889
98	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0		M.P. 55-57°C
99	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0		M.P. 120-121°C
100	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0		n_D^{28} 1.5371
101	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0		$n_D^{28.5}$ 1.5349
102	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0		M.P. 102-103°C

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(Continued)

Compound No.	R ¹	R ²	R ³	X	Y	Z	Physical constant
103	-C ₂ H ₅	-C ₂ H ₅	CH ₃ -CHCH ₂ OCCH ₃	0	0	-COC ₂ H ₅	n _D ²⁷ 1.4972
104	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	-SOCH ₃	M.P. 114-115°C
105	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	0	0	-CH ₂ COOC ₂ H ₅	n _D ^{27.5} 1.4948
106	-C ₂ H ₅	-C ₂ H ₅	-C ₂ H ₅	S	0	H	M.P. 74-75°C
107	-C ₂ H ₅	-C ₂ H ₅	-CH ₃	S	0	H	M.P. 87-88°C
108	-C ₂ H ₅	-C ₂ H ₅	-C ₄ H ₉ (sec)	0	S	H	M.P. 97-98°C
109	-C ₂ H ₅	-C ₂ H ₅	-C ₃ H ₇ (iso)	S	S	H	M.P. 64-65°C

In the practical usage of the N-phenylcarbamates (I) as fungicides, they may be applied as such or in a preparation form such as dusts, wettable powders, oil sprays, emulsifiable concentrates, tablets, granules, fine granules, aerosols or flowables. Such preparation form can be prepared in a conventional manner by mixing at least one of the N-phenylcarbamates (I) with an appropriate solid or liquid carrier(s) or diluent(s) and, if necessary, an appropriate adjuvant(s) (e.g. surfactants, adherents, dispersants, stabilizers) for improving the dispersibility and other properties of the active ingredient(s).

Examples of the solid carriers or diluents are botanical materials (e.g. flour, tobacco stalk powder, soybean powder, walnut-shell powder, vegetable powder, saw dust, bran, bark powder, cellulose powder, vegetable extract residue), fibrous materials (e.g. paper, corrugated cardboard, old rags), synthetic plastic powders, clays (e.g. kaolin, bentonite, fuller's earth), talcs, other inorganic materials (e.g. pyrophyllite, sericite, pumice, sulfur powder, active carbon) and chemical fertilizers (e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, urea, ammonium chloride).

Examples of the liquid carriers or diluents are water, alcohols (e.g. methanol, ethanol), ketones (e.g. acetone, methylethylketone), ethers (e.g. diethyl ether, dioxane, cellosolve, tetrahydrofuran), aromatic hydrocarbons (e.g. benzene, toluene, xylene, methyl naphthalene),

aliphatic hydrocarbons (e.g. gasoline, kerosene, lamp oil), esters, nitriles, acid amides (e.g. dimethylformamide, dimethylacetamide), halogenated hydrocarbons (e.g. dichloroethane, carbon tetrachloride), etc.

5 Examples of the surfactants are alkyl sulfuric esters, alkyl sulfonates, alkylaryl sulfonates, polyethylene glycol ethers, polyhydric alcohol esters, etc. Examples of the adherents and dispersants may include casein, gelatin, starch powder, carboxymethyl cellulose, gum arabic, alginic
10 acid, lignin, bentonite, molasses, polyvinyl alcohol, pine oil and agar. As the stabilizers, there may be used PAP (isopropyl acid phosphate mixture), TCP (tricresyl phosphate), tolu oil, epoxydized oil, various surfactants, various fatty acids and their esters, etc.

15 The foregoing preparations generally contain at least one of the N-phenylcarbamates (I) in a concentration of about 1 to 95 % by weight, preferably of 2.0 to 80 % by weight. By using the preparations, the N-phenylcarbamates (I) are generally applied in such amounts as 2 to 100 g per
20 10 are.

 When only the drug-resistant strains of phytopathogenic fungi are present, the N-phenylcarbamates (I) may be used alone. However, when the drug-sensitive strains are present together with the drug-resistant strains, their
25 alternate use with benzimidazole thiophanate fungicides and/or cyclic imide fungicides or their combined use with benzimidazole thiophanate fungicides and/or cyclic imide

fungicides is favorable. In such alternate or combined use, each active ingredient may be employed as such or in conventional agricultural preparation forms. In case of the combined use, the weight proportion of the N-phenylcarbamate (I) and the benzimidazole thiophanate fungicide and/or the cyclic imide fungicide may be from about 1 : 0.1 to 1 : 10.0.

Typical examples of the benzimidazole thiophanate fungicides and the cyclic imide fungicides are shown in Table 2.

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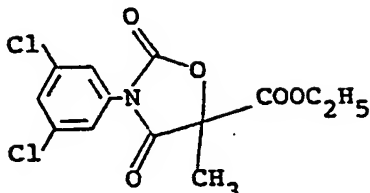
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Table 2

Compound	Structure	Name
A		Methyl 1-(butylcarbamoyl)benzimidazol-2-ylcarbamate
B		2-(4-Thiazolyl)benzimidazole
C		Methyl benzimidazol-2-ylcarbamate
D		2-(2-Furyl)benzimidazole
E		1,2-Bis(3-methoxycarbonyl-2-thio-ureido)benzene
F		1,2-Bis(3-ethoxycarbonyl-2-thio-ureido)benzene

<u>Compound</u>	<u>Structure</u>	<u>Name</u>
G		2-(O,S-Dimethylphosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene
H		2-(O,O-Dimethylthiophosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene
I		N-(3',5'-Dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide
J		3-(3',5'-Dichlorophenyl)-1-isopropylcarbamoylimidazolidin-2,4-dione
K		3-(3',5'-Dichlorophenyl)-5-methyl-5-vinylloxazolidin-2,4-dione

Compound	Structure	Name
L		Ethyl (RS)-3-(3',5'-dichlorophenyl)-5-methyl-2,4-dioxo-oxazolidine-5-carboxylate

5

Besides, the N-phenylcarbamates (I) may be also used in admixture with other fungicides, herbicides, insecticides, miticides, fertilizers, etc.

When the N-phenylcarbamates (I) are used as fungicides, they may be applied in such amounts as 2 to 100 grams per 10 ares. However, this amount may vary depending upon preparation forms, application times, application methods, application sites, diseases, crops and so on, and therefore, they are not limited to said particular amounts.

Some practical embodiments of the fungicidal composition according to the invention are illustratively shown in the following Examples wherein % and part(s) are by weight.

Preparation Example 1

Two parts of Compound No. 21, 88 parts of clay and 10 parts of talc were thoroughly pulverized and mixed together to obtain a dust preparation containing 2 % of the active ingredient.

Preparation Example 2

Thirty parts of Compound No. 11, 45 parts of diatomaceous earth, 20 parts of white carbon, 3 parts of sodium laurylsulfate as a wetting agent and 2 parts of

calcium ligninsulfonate as a dispersing agent were mixed while being powdered to obtain a wettable powder preparation containing 30 % of the active ingredient.

Preparation Example 3

5 Fifty parts of Compound No. 13, 45 parts of diatomaceous earth, 2.5 parts of calcium alkylbenzene-sulfonate as a wetting agent and 2.5 parts of calcium ligninsulfonate as a dispersing agent were mixed while being powdered to obtain a wettable powder preparation containing
10 50 % of the active ingredient.

Preparation Example 4

Ten parts of Compound No. 46, 80 parts of cyclohexanone and 10 parts of polyoxyethylene alkylaryl ether as an emulsifier were mixed together to obtain an
15 emulsifiable concentrate preparation containing 10 % of the active ingredient.

Preparation Example 5

One part of Compound No. 7, 1 part of Compound I, 88 parts of clay and 10 parts of talc were thoroughly
20 pulverized and mixed together to obtain a dust preparation containing 2 % of the active ingredient.

Preparation Example 6

Twenty parts of Compound No. 86, 10 parts of Compound J, 45 parts of diatomaceous earth, 20 parts of
25 white carbon, 3 parts of sodium laurylsulfate as a wetting agent and 2 parts of calcium ligninsulfonate as a dispersing

agent were mixed while being powdered to obtain a wettable powder preparation containing 30 % of the active ingredient.

Preparation Example 7

Ten parts of Compound No. 88, 40 parts of
5 Compound B, 45 parts of diatomaceous earth, 2.5 parts of calcium alkylbenzenesulfonate as a wetting agent and 2.5 parts of calcium ligninsulfonate as a dispersing agent were mixed while being powdered to obtain a wettable powder preparation containing 50 % of the active ingredient.

10 Preparation Example 8

Twenty-five parts of Compound No. 94, 50 parts of Compound I, 18 parts of diatomaceous earth, 3.5 parts of calcium alkylbenzenesulfonate as a wetting agent and 3.5 parts of calcium ligninsulfonate as a dispersing agent were
15 mixed while being powdered to obtain a wettable powder preparation containing 75 % of the active ingredient.

Preparation Example 9

Twenty parts of Compound No. 50, 30 parts of Compound A, 40 parts of powdery sucrose, 5 parts of white
20 carbon, 3 parts of sodium laurylsulfate as a wetting agent and 2 parts of calcium ligninsulfonate as a dispersing agent were mixed while being powdered to obtain a wettable powder preparation containing 50 % of the active ingredient.

Typical test data indicating the excellent fungi-
25 cidal activity of the N-phenylcarbamates (I) are shown below. The compounds used for comparison are as follows:

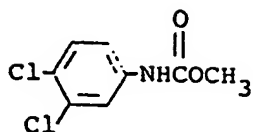
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Compound

Remarks

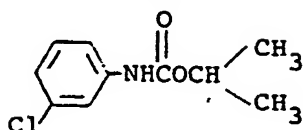
Swept

Commercially available
herbicide



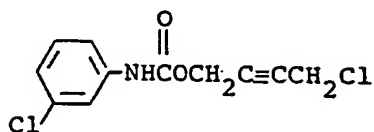
Chlorpropham

Commercially available
herbicide



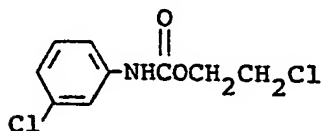
Barban

Commercially available
herbicide



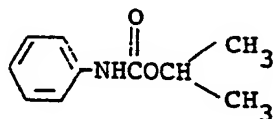
CEPC

Commercially available
herbicide



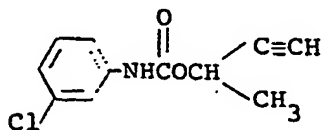
Propham

Commercially available
herbicide



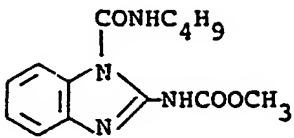
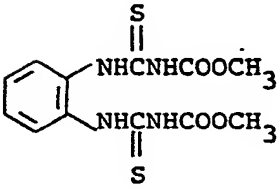
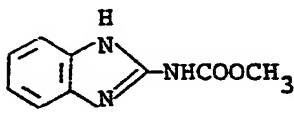
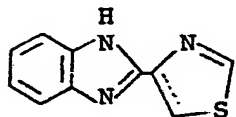
Chlorbufam

Commercially available
herbicide



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<u>Compound</u>	<u>Remarks</u>
<u>Benomyl</u> 	Commercially available fungicide
<u>Thiophanate-methyl</u> 	Commercially available fungicide
<u>Carbendazim</u> 	Commercially available fungicide
<u>Thiabendazole</u> 	Commercially available fungicide

Experiment 1

Protective activity test on powdery mildew of cucumber (Sphaerotheca fuliginea):-

A flower pot of 90 ml volume was filled with sandy soil, and seeds of cucumber (var: Sagami-hanjiro) were sowed therein. Cultivation was carried out in a greenhouse for 8 days. Onto the resulting seedlings having cotyledons, the test compound formulated in emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate

of 10 ml per pot. Then, the seedlings were inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of Sphaerotheca fuliginea by spraying and further cultivated in the greenhouse. Ten days thereafter, the infectious state of the plants was observed. The degree of damage was determined in the following manner, and the results are shown in Table 3.

The leaves examined were measured for a percentage of infected area and classified into the corresponding disease indices, 0, 0.5, 1, 2, 4:

<u>Disease index</u>	<u>Percentage of infected area</u>
0	No infection
0.5	Infected area of less than 5 %
1	Infected area of less than 20 %
2	Infected area of less than 50 %
4	Infected area of not less than 50 %

The disease severity was calculated according to the following equation:

$$\text{Disease severity (\%)} = \frac{\sum (\text{Disease index}) \times (\text{Number of leaves})}{4 \times (\text{Total number of leaves examined})} \times 100$$

The prevention value was calculated according to the following equation:

$$\text{Prevention value (\%)} = 100 - \frac{(\text{Disease severity in treated plot})}{(\text{Disease severity in untreated plot})} \times 100$$

Table 3

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
1	200	100	0
2	200	100	0
3	200	100	0
4	200	92	0
5	200	100	0
6	200	100	0
7	200	100	32
8	200	100	0
9	200	100	0
10	200	100	0
11	200	100	0
12	200	100	0
13	200	100	0
14	200	100	0
15	200	100	0
16	200	100	0
17	200	100	0
18	200	100	0
19	200	100	0
20	200	100	0
21	200	100	0
22	200	100	0
23	200	90	0
24	200	100	0
25	200	100	0
26	200	100	0
27	200	100	0
28	200	100	0
29	200	100	0
30	200	100	0
31	200	100	0
32	200	100	0
33	200	84	0
34	200	100	0
35	200	100	26
36	200	97	0
37	200	100	0
38	200	100	34
39	200	100	0
40	200	100	0
41	200	100	0
42	200	82	0

(Continued)

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
43	200	100	0
44	200	100	0
45	200	100	0
46	200	100	0
47	200	100	0
48	200	100	0
49	200	100	0
50	200	100	0
51	200	100	0
52	200	100	0
53	200	100	0
54	200	100	0
55	200	90	0
56	200	100	0
57	200	100	0
58	200	100	0
59	200	100	0
60	200	100	0
61	200	100	0
62	200	100	0
63	200	100	0
64	200	100	0
65	200	86	0
66	200	100	0
67	200	100	52
68	200	100	23
69	200	88	0
70	200	100	0
71	200	100	0
72	200	100	0
73	200	100	0
74	200	100	0
75	200	100	0
76	200	100	0
77	200	90	0
78	200	92	0
79	200	94	0
80	200	100	0
81	200	100	0
82	200	100	0
83	200	100	0
84	200	97	0
85	200	94	0

(Continued)

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
86	200	100	0
87	200	100	0
88	200	100	0
89	200	92	0
90	200	88	0
91	200	84	0
92	200	88	0
93	200	90	0
94	200	100	0
95	200	100	0
96	200	100	0
97	200	100	0
98	200	100	0
99	200	100	0
100	200	100	0
101	200	98	0
102	200	100	0
103	200	100	0
104	200	86	0
105	200	84	0
106	200	94	0
107	200	90	0
108	200	88	0
109	200	88	0
Swep	200	0	0
Chlorpropham	200	0	0
Barban	200	25	0
CEPC	200	0	0
Propham	200	0	0
Chlorbufam	200	0	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100
Carbendazim	200	0	100

As understood from the results shown in Table 3, the N-phenylkcarbamates (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-

sensitive strain. To the contrary, commercially available known fungicides such as Benomyl, Thiophanate-methyl and Carbendazim show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

- 5 Other tested compounds structurally similar to the N-phenyl-carbamates (I) do not show any fungicidal activity on the drug-sensitive strain and the drug-resistant strain.

Experiment 2

- Preventive effect on cercospora leaf spot of
10 sugarbeet (Cercospora beticola):-

- A flower pot of 90 ml volume was filled with sandy soil, and seeds of sugarbeet (var: Detroit dark red) were sowed therein. Cultivation was carried out in a greenhouse for 20 days. Onto the resulting seedlings, the test
15 compound formulated in emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per pot. Then, the seedlings were inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of Cercospora beticola by spraying. The pot was covered with a
20 polyvinyl chloride sheet to make a condition of high humidity, and cultivation was continued in the greenhouse for 10 days. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 4.

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Table 4

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
2	200	100	0
11	200	100	0
12	200	100	0
13	200	100	0
14	200	100	0
15	200	100	0
16	200	100	0
17	200	100	0
21	200	100	0
24	200	100	0
25	200	100	0
27	200	100	0
28	200	100	0
30	200	100	0
31	200	100	0
32	200	100	0
35	200	100	0
36	200	100	0
38	200	100	0
39	200	100	0
40	200	100	0
42	200	88	0
43	200	94	0
46	200	100	0
50	200	97	0
52	200	100	0
53	200	100	0
56	200	100	0
60	200	100	0
61	200	100	0
62	200	100	0
68	200	100	0
73	200	100	0
75	200	100	0
76	200	100	0
80	200	100	0
81	200	100	0
83	200	100	0
86	200	100	0
87	200	100	0
88	200	100	0
94	200	100	0
95	200	100	0

(Continued)

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
96	200	97	0
98	200	100	0
99	200	100	0
100	200	100	0
101	200	100	0
102	200	100	0
Sweep	200	0	0
Chlorpropham	200	0	0
Barban	200	34	0
CEPC	200	0	0
Propham	200	0	0
Chlorbufam	200	0	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100
Carbendazim	200	0	100

As understood from the results shown in Table 4, the N-phenylcarbamates (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain. Other tested compounds structurally similar to the N-phenylcarbamates (I) do not show any fungicidal activity on the drug-sensitive strain and the drug-resistant strain.

Experiment 3

Preventive effect on scab of pear (Venturia nashicola):-

A plastic pot of 90 ml volume was filled with sandy soil, and seeds of pear (var: Chojuro) were sowed therein. Cultivation was carried out in a greenhouse for 20 days. Onto the resulting seedlings, the test compound formulated in emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per pot. Then, the seedlings were inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of Venturia nashicola by spraying. The resulting plants were placed at 20°C under a condition of high humidity for 3 days and then at 20°C under irradiation with a fluorescent lamp for 20 days. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 5.

Table 5

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
2	200	100	0
3	200	100	0
7	200	100	0
11	200	100	0
12	200	100	0
13	200	100	0
14	200	100	0
15	200	100	0
16	200	100	0
17	200	100	0

(Continued)

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
21	200	100	0
24	200	100	0
25	200	100	0
27	200	100	0
28	200	100	0
35	200	100	0
36	200	97	0
42	200	91	0
43	200	100	0
46	200	100	0
50	200	100	0
53	200	100	0
56	200	100	0
68	200	100	0
75	200	100	0
76	200	97	0
80	200	100	0
81	200	100	0
83	200	97	0
86	200	100	0
87	200	100	0
88	200	100	0
94	200	100	0
95	200	97	0
96	200	94	0
97	200	97	0
98	200	100	0
99	200	100	0
100	200	100	0
101	200	97	0
102	200	100	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 5, the N-phenylcarbamates (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive

strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

5 Experiment 4

Preventive effect on brown leaf-spot of peanut
(Cercospora arachidicola):-

10 A plastic pot of 90 ml volume was filled with
sandy soil, and seeds of peanut (var: Chiba hanryusei) were
sowed therein. Cultivation was carried out in a greenhouse
for 14 days. Onto the resulting seedlings, the test
compound formulated in emulsifiable concentrate or wettable
powder and diluted with water was sprayed at a rate of 10 ml
per pot. Then, the seedlings were inoculated with a spore
15 suspension of the drug-resistant or drug-sensitive strain of
Cercospora arachidicola by spraying. The resulting plants
were covered with a polyvinyl chloride sheet to make a
condition of humidity and cultivated in the greenhouse for
10 days. The degree of damage was determined in the same
20 manner as in Experiment 1, and the results are shown in
Table 6.

Table 6

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
2	200	100	0
7	200	100	0
12	200	100	0
13	200	100	0
17	200	100	0
25	200	100	0
27	200	100	0
28	200	100	0
31	200	100	0
32	200	100	0
35	200	100	0
38	200	100	0
39	200	100	0
40	200	100	0
46	200	100	0
50	200	100	0
53	200	100	0
56	200	100	0
60	200	100	0
62	200	100	0
64	200	100	0
73	200	100	0
76	200	100	0
86	200	100	0
87	200	100	0
88	200	100	0
94	200	100	0
98	200	100	0
99	200	100	0
100	200	100	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 6, the N-phenylcarbamates (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive

strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

5 Experiment 5

Preventive effect on gray mold of cucumber
(Botrytis cinerea):-

Plastic pots of 90 ml volume was filled with sandy soil, and seeds of cucumber (var: Sagami-hanjiro) were
10 sowed therein. Cultivation was carried out in a greenhouse for 8 days to obtain cucumber seedlings expanding cotyledons. Onto the resulting seedlings, the test compound formulated in emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per
15 pot. After air-drying, the seedlings were inoculated with mycelial disks (5 mm in diameter) of the drug-resistant or drug-sensitive strain of Botrytis cinerea by putting them on the leaf surfaces. After the plants were infected by incubating under high humidity at 20°C for 3 days, the rates
20 of disease severity were observed. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 7.

Table 7

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
1	200	100	0
	50	94	0
2	200	100	0
	50	100	0
3	200	100	0
	50	94	0
4	500	98	0
5	200	100	0
6	200	91	0
7	200	100	0
	50	97	0
8	200	100	0
9	200	100	0
10	500	98	0
11	200	97	0
12	200	100	0
	50	97	0
13	200	100	0
	50	100	0
	12.5	100	0
14	200	100	0
	50	100	0
15	200	100	0
	50	100	0
	12.5	100	0
16	200	100	0
	50	100	0
17	200	100	0
	50	100	0
18	200	97	0
19	200	100	0
20	200	100	0
21	200	100	0
	50	100	0
22	200	97	0
23	500	96	0
24	200	100	0
25	200	100	0
	50	100	0
	12.5	100	0
26	200	100	0

(Continued)

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
27	200	100	0
	50	100	0
28	200	100	0
	50	100	0
	12.5	94	0
29	200	100	0
	50	100	0
30	200	100	0
	50	100	0
31	200	100	0
	50	100	0
32	200	100	0
	50	100	0
33	500	86	0
34	200	100	0
35	200	100	0
	50	100	0
36	200	100	0
37	200	100	0
38	200	100	0
	50	100	0
39	200	100	0
	50	100	0
40	200	100	0
	50	100	0
41	200	94	0
42	500	82	0
43	200	100	0
	50	100	0
	12.5	94	0
44	200	100	0
45	200	91	0
46	200	100	0
	50	100	0
47	200	100	0
48	200	100	0
49	200	100	0
50	200	100	0
	50	100	0
51	200	100	0
	50	100	0
52	200	100	0
	50	100	0

(Continued)

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
53	200	100	0
	50	100	0
54	200	95	0
55	500	97	0
56	200	100	0
	50	100	0
57	200	97	0
58	200	97	0
59	200	100	0
60	200	100	0
61	200	100	0
	50	100	0
62	200	100	0
	50	100	0
63	200	100	0
	50	100	0
64	200	100	0
	50	100	0
65	500	87	0
66	200	100	0
67	200	100	0
68	200	100	0
69	500	95	0
70	200	100	0
71	200	97	0
72	200	97	0
73	200	97	0
74	200	100	0
75	200	100	0
76	200	100	0
77	500	97	0
78	200	100	0
79	200	100	0
80	200	100	0
81	200	100	0
82	200	100	0
83	200	100	0
	50	92	0
84	200	100	0
85	200	97	0
86	200	100	0
	50	100	0
	12.5	97	0

(Continued)

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
87	200	100	0
	50	97	0
	12.5	86	0
88	200	100	0
	50	100	0
	12.5	88	0
89	200	94	0
90	200	88	0
91	200	92	0
92	200	92	0
93	200	94	0
94	200	100	0
	50	97	0
	12.5	94	0
95	200	100	0
	50	97	0
96	200	100	0
	50	94	0
97	200	100	0
	50	94	0
98	200	100	0
	50	100	0
	12.5	97	0
99	200	100	0
	50	97	0
	12.5	94	0
100	200	100	0
	50	97	0
	12.5	97	0
101	200	100	0
	50	94	0
102	200	100	0
	50	97	0
103	200	100	0
	50	94	0
104	200	97	0
105	200	97	0
106	200	100	0
107	200	100	0
108	200	100	0
109	200	97	0

(Continued)

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
5 Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 7, the N-phenylcarbamates (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

15 Experiment 6

Preventive effect on gummy stem blight of cucumber (Mycosphaerella melonis):-

Plastic pots of 90 ml volume was filled with sandy soil, and seeds of cucumber (var.: Sagami-hanjiro) were sowed therein. Cultivation was carried out in a greenhouse for 8 days to obtain cucumber seedlings expanding cotyledons. Onto the resulting seedlings, the test compound formulated in emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per pot. After air-drying, the seedlings were inoculated with mycelial disks (5 mm in diameter) of the drug-resistant or

drug-sensitive strain of Mycosphaerella melonis by putting them on the leaf surfaces. After the plants were infected by incubating under high humidity at 25°C for 4 days, the rates of disease severity were observed. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 8.

Table 8

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
3	200	100	0
7	200	100	0
12	200	100	0
13	200	100	0
14	200	100	0
16	200	100	0
28	200	100	0
36	200	100	0
46	200	100	0
48	200	100	0
49	200	100	0
53	200	100	0
56	200	100	0
61	200	100	0
63	200	100	0
74	200	100	0
76	200	100	0
86	200	100	0
87	200	100	0
88	200	100	0
94	200	100	0
98	200	100	0
99	200	100	0
100	200	100	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 8, the N-phenylcarbamates (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

Experiment 7

10 Preventive effect on green mold of orange
(Penicillium italicum):-

Fruits of orange (var: Unshu) were washed with water and dried in the air. The fruits were immersed in a solution of the test compound prepared by diluting an emulsifiable concentrate comprising the test compound with water for 1 minute. After drying in the air, the fruits were inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of Penicillium italicum by spraying and placed in a room of high humidity for 14 days. The degree of damage was determined in the following manner:

The fruits examined were measured for a percentage of infected area and classified into the corresponding indices, 0, 1, 2, 3, 4, 5:

<u>Disease index</u>	<u>Percentage of infected area</u>
0	No infection
1	Infected area of less than 20 %
2	Infected area of less than 40 %
3	Infected area of less than 60 %
4	Infected area of less than 80 %
5	Infected area of not less than 80 %

Calculation of the degree of damage and the prevention value was made as in Experiment 1.

The results are shown in Table 9.

Table 9

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
2	200	100	0
5	200	100	0
9	200	100	0
11	200	100	0
13	200	100	0
21	200	100	0
28	200	97	0
46	200	100	0
50	200	100	0
53	200	100	0
56	200	100	0
61	200	100	0
62	200	100	0
63	200	100	0
64	200	100	0
67	200	100	0
70	200	100	0
73	200	100	0
74	200	100	0
75	200	100	0
76	200	100	0
86	200	100	0
87	200	100	0
88	200	100	0
94	200	100	0
98	200	100	0
99	200	100	0
100	200	100	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100
Thiabendazole	200	0	100

As understood from the results shown in Table 9, the N-phenylcarbamates (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive

strain. To the contrary, commercially available known fungicides such as Benomyl, Thiophanate-methyl and Thia-bendazole show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

5 Experiment 8

Preventive effect on powdery mildew of cucumber
(Sphaerotheca fuliginea):-

A plastic pot of 90 ml volume was filled with sandy soil, and seeds of cucumber (var: Sagami-hanjiro)
10 were sowed therein. Cultivation was carried out in a greenhouse for 8 days. Onto the resulting seedlings having cotyledons, the test compound(s) formulated in emulsifiable concentrate or wettable powder and diluted with water were sprayed at a rate of 10 ml per pot. Then, the seedlings
15 were inoculated with a mixed spore suspension of the drug-resistant and drug-sensitive strain of Sphaerotheca fuliginea by spraying and further cultivated in the greenhouse. Ten days thereafter, the infectious state of the plants was observed. The degree of damage was
20 determined in the same manner as in Experiment 1, and the results are shown in Table 10.

Table 10

Compound No.	Concentration of active ingredient (ppm)	Prevention value (%)
13	100	34
13	20	0
15	100	28
15	20	0
28	100	44
28	20	0
43	100	36
43	20	0
86	100	44
86	20	0
88	100	28
88	20	0
94	100	32
94	20	0
98	100	28
98	20	0
99	100	28
99	20	0
100	100	36
100	20	0
A	100	45
A	20	12
B	500	42
B	100	10
C	100	42
C	20	8
D	500	36
D	100	0
E	100	44
E	20	10

(Continued)

Compound No.	Concentration of active ingredient (ppm)	Prevention value (%)
F	100	43
F	20	8
G	100	42
G	20	8
H	100	40
H	20	5
13 + A	20 + 20	100
13 + E	20 + 20	100
13 + H	20 + 20	100
15 + A	20 + 20	100
15 + F	20 + 20	100
28 + A	20 + 20	100
28 + B	20 + 20	100
28 + C	20 + 20	100
43 + D	20 + 20	100
43 + G	20 + 20	100
43 + H	20 + 20	100
86 + A	20 + 20	100
86 + B	20 + 20	100
86 + F	20 + 20	100
88 + C	20 + 20	100
88 + E	20 + 20	100
88 + G	20 + 20	100
94 + A	20 + 20	100
94 + E	20 + 20	100
94 + G	20 + 20	100
98 + C	20 + 20	100
98 + H	20 + 20	100
99 + A	20 + 20	100
99 + B	20 + 20	100
100 + A	20 + 20	100
100 + D	20 + 20	100
100 + E	20 + 20	100

As understood from the results shown in Table 10, the combined use of the N-phenylcarbamates (I) of the invention with benzimidazole thiophanate fungicides and/or cyclic imide fungicides show much more excellent preventive effect than their sole use.

Experiment 9

Preventive effect on gray mold of tomato (Botrytis cinerea):-

A plastic pot of 90 ml volume was filled with sandy soil, and seeds of tomato (var: Fukuji No. 2) were sowed therein. Cultivation was carried out in a greenhouse for 4 weeks. Onto the resulting seedlings at the 4-leaf stage, the test compound(s) formulated in emulsifiable concentrate or wettable powder and diluted with water were sprayed at a rate of 10 ml per pot. Then, the seedlings were inoculated with a mixed spore suspension of the drug-resistant and drug-sensitive strain of Botrytis cinerea by spraying and placed at 20°C in a room of high humidity for 5 days. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 11.

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Table 11

Compound No.	Concentration of active ingredient (ppm)	Prevention value (%)
13	100	44
13	20	0
25	100	27
25	20	0
28	100	38
28	20	0
43	100	38
43	20	0
86	100	42
86	20	0
88	100	42
88	20	0
94	100	42
94	20	0
98	100	40
98	20	0
99	100	44
99	20	0
100	100	38
100	20	0
I	100	48
I	20	22
J	500	46
J	100	18
K	100	42
K	20	15
L	500	42
L	100	12

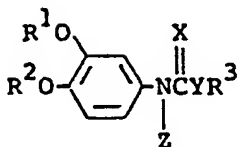
(Continued)

Compound No.	Concentration of active ingredient (ppm)	Prevention value (%)
13 + I	20 + 50	100
13 + J	20 + 50	100
13 + K	20 + 50	100
13 + L	20 + 50	100
25 + I	20 + 50	100
25 + K	20 + 50	100
28 + I	20 + 50	100
28 + L	20 + 50	100
43 + I	20 + 50	100
43 + J	20 + 50	100
86 + I	20 + 50	100
86 + K	20 + 50	100
88 + I	20 + 50	100
88 + J	20 + 50	100
94 + I	20 + 50	100
94 + J	20 + 50	100
98 + I	20 + 50	100
98 + K	20 + 50	100
99 + I	20 + 50	100
99 + J	20 + 50	100
100 + I	20 + 50	100
100 + K	20 + 50	100

As understood from the results shown in Table 11, the combined use of the N-phenylcarbamates (I) of the invention with benzimidazole thiophanate fungicides and/or cyclic imide fungicides show much more excellent preventive effect than their sole use.

CLAIMS:

1. An N-phenylcarbamate of the formula:



wherein R^1 and R^2 are the same or different and are each independently a lower alkyl group, a lower alkenyl group, a lower alkynyl group or a lower alkyl group substituted with at least one halogen atom, lower alkoxy or lower cycloalkyl group; R^3 is a C_1 - C_8 alkyl group, a C_3 - C_8 alkenyl group, a C_6 - C_8 alkynyl group, a lower cycloalkyl group, a lower haloalkenyl group, a lower haloalkynyl group, a lower aralkyl group, a lower alkyl group substituted with at least one halogen atom, cyano, lower alkoxy, lower alkenyloxy, lower haloalkoxy, phenoxy, lower aralkyloxy or lower cycloalkyl group,

10

15

or a group of the formula:

$$\begin{array}{c} (\text{CH}_2)_m \\ \diagup \quad \diagdown \\ -\text{CH} \quad \text{O} \\ \diagdown \quad \diagup \\ (\text{CH}_2)_n \end{array}$$

in which m is 0, 1

20 or 2, n is 1, 2 or 3; X and Y are the same or different and each represent an oxygen atom or a sulfur atom; and Z is a hydrogen atom, a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a lower cycloalkyl group, a lower haloalkenyl group, a lower alkyl group substituted with at least one halogen atom, cyano, lower alkoxy or lower alkoxy carbonyl group, or a group of the formula:

25

-COR⁴ or -SO₂R⁴ in which R⁴ is a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a lower cycloalkyl group, a lower haloalkenyl group, a lower alkyl group substituted with at least one halogen atom, cyano, lower alkoxy, lower cycloalkyl or phenoxy group (the phenoxy group optionally being substituted with at least one halogen atom and/or at least one alkyl group), a phenyl group, a furyl group, a thienyl group, a phenyl group substituted with at least one halogen atom, cyano, nitro, trifluoromethyl, lower alkyl or lower alkoxy group, or an aralkyl group (the aralkyl group optionally being substituted with at least one halogen atom and/or at least one alkyl group), with the proviso that when R¹ is methyl, R² is not methyl or butyl.

15

2. An N-phenylcarbamate as claimed in claim 1 wherein R¹ and R² are each independently methyl, ethyl, n-propyl, isopropyl, n-butyl, allyl, 2-butenyl, 3-butenyl, propargyl, 3-butynyl, difluoromethyl, 2-chloroethyl, 2,2,2-trifluoroethyl, 2-methoxyethyl or cyclopropylmethyl, R³ is methyl, ethyl, n-propyl, isopropyl, sec-butyl, 1-ethylpropyl, 1-methylbutyl, 1-ethylbutyl, 2-butenyl, 3-butenyl, 2-methyl-2-propenyl, 1-ethyl-2-propenyl, 1-methyl-3-butenyl, 1-pentyl-2-propenyl, propargyl, 1-methyl-2-propynyl, 2-butynyl, 3-butynyl, 1-ethyl-2-propynyl, 1-methyl-3-butynyl, 1-butyl-2-propynyl, 1-pentyl-2-propynyl, cyclobutyl, cyclo-

25

pentyl, 2-fluoroethyl, 2-chloroethyl, 2,2-dichloroethyl,
1-methyl-2-bromoethyl, 1-fluoromethyl-2-fluoroethyl,
1-bromomethyl-2-bromoethyl, 1-methyl-2,2,2-trichloroethyl,
1-ethyl-2-bromoethyl, 4-chloro-2-butenyl, 4-chloro-2-
5 butynyl, 2-cyanoethyl, 1-methyl-2-methoxyethyl, 1-methyl-2-
butoxyethyl, 2-allyloxyethyl, 2-(2-chloroethoxy)ethyl,
2-benzyloxyethyl, 1-chloroethyl-2-methoxyethyl, cyclopropyl-
methyl, 1-cyclopropylethyl, 1-cyclopentylethyl, 2-furyl-
methyl, 1-phenylethyl or 3-tetrahydrofuranyl; X and Y are
10 independently oxygen or sulfur; and Z is hydrogen, methyl,
ethyl, n-butyl, allyl, acetyl, propionyl, n-butanoyl,
sec-butanoyl, cyclopropanecarbonyl, benzoyl, 2-chloro-
benzoyl, 2,4-dichlorobenzoyl, 4-methylbenzoyl, methane-
sulfonyl or ethoxycarbonylmethyl, with the proviso that when
15 R^1 is methyl, R^2 is not methyl or butyl.

3. An N-phenylcarbamate as claimed in claim 2
wherein R^1 and R^2 are each independently methyl, ethyl, n-propyl,
allyl or propargyl, R^3 is ethyl, isopropyl, sec-butyl,
20 1-methylbutyl, 1-ethylpropyl, 1-ethylbutyl, 1-methyl-2-
propenyl, 1-ethyl-2-propenyl, 1-methyl-3-butenyl, propargyl,
1-methyl-2-propynyl, 1-ethyl-2-propynyl, 3-butyne, 1-
methyl-3-butyne, 1-butyl-2-propynyl, 2-fluoroethyl, 1-
methyl-2-bromoethyl, 1-fluoromethyl-2-fluoroethyl, 1-bromo-
25 methyl-2-bromoethyl, 4-chloro-2-butyne, 1-methyl-2-methoxy-
ethyl, 1-cyclopropylethyl or 1-phenylethyl; X is oxygen, Y
is oxygen or sulfur; and Z is hydrogen, acetyl, propionyl,

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n-butanoyl, sec-butanoyl, cyclopropanecarbonyl, benzoyl, 2-chlorobenzoyl, 2,4-dichlorobenzoyl or 4-methylbenzoyl, with the proviso that when R^1 is methyl, R^2 is not methyl.

5 4. An N-phenylcarbamate as claimed in claim 3 wherein R^1 and R^2 are each ethyl, R^3 is ethyl, isopropyl, sec-butyl, 1-methylbutyl, 1-ethylbutyl, 1-ethyl-3-butenyl, 1-methyl-2-propynyl, 4-chloro-2-butyne or 1-phenylethyl, X is oxygen, Y is oxygen or sulfur and Z is hydrogen, acetyl, 10 cyclopropanecarbonyl, benzoyl or 2-chlorobenzoyl.

5. A compound as claimed in claim 1 which is isopropyl N-(3,4-diethoxyphenyl)carbamate, 1-methyl-2-propynyl N-(3,4-diethoxyphenyl)-carbamate, 4-chloro-2-butyne N-(3,4- 15 diethoxyphenyl)-carbamate, isopropyl N-(3,4-diethoxyphenyl) thiolcarbamate, 1-phenylethyl N-(3,4-diethoxyphenyl)carbamate, isopropyl N-acetyl-N-(3,4-diethoxyphenyl)-carbamate, isopropyl N-cyclopropanecarbonyl-N-(3,4-diethoxyphenyl)carbamate, isopropyl N-benzoyl-N-(3,4-diethoxyphenyl)-carbamate or 20 isopropyl N-(2-chlorobenzoyl)-N(3,4-diethoxyphenyl)carbamate.

6. A fungicidal composition which comprises as an active ingredient a fungicidally effective amount of an N-phenylcarbamate as claimed in any one of claims 1 to 5 together with an inert carrier or diluent. 25

7. A fungicidal composition as claimed in claim

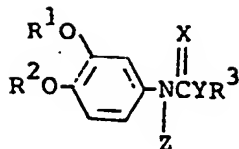
6 which further comprises as an additional active ingredient(s) a benzimidazole thiophanate fungicide and/or a cyclic imide fungicide.

5 8. A fungicidal composition as claimed in claim 7 wherein the benzimidazol thiophanate fungicide is methyl 1-(butylcarbamoyl)benzimidazol-2-ylcarbamate, 2-(2-furyl)benzimidazole, 2-(4-thiazolyl)benzimidazole, methyl benzimidazol-2-ylcarbamate, 1,2,-bis(3-methoxycarbonyl-2-thioureido)benzene, 1,2-bis(3-ethoxycarbonyl-2-thioureido)-
10 thioureido)benzene, 1,2-bis(3-ethoxycarbonyl-2-thioureido)-benzene, 2-(O,S-dimethylphosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene or 2-(O,O-dimethylthiophosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene.

15 9. A fungicidal composition as claimed in claim 7 wherein the cyclic imide fungicide is 3-(3',5'-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, 3-(3',5'-dichlorophenyl)-1-isopropylcarbamoylimidazolidine-2,4-dione, 3-3',5'-dichlorophenyl)-5-methyl-5-vinyloxazoline-2,4-dione or ethyl (RS)-3-(3',5'-dichlorophenyl)-5-methyl-2,4-dioxooxazolidine-5-carboxylate.
20

 10. A method for controlling plant pathogenic
25 fungi which comprises applying a fungicidally effective amount of at least one N-phenylcarbamates of the formula:

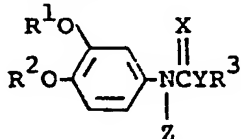
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wherein R^1 , R^2 , R^3 , X, Y and Z are each as defined in claim
5 1, to plant pathogenic fungi.

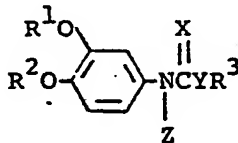
11. A method as claimed in claim 10 wherein the
plant pathogenic fungi is the drug-resistant strain.

10 12. A method for controlling plant pathogenic
fungi which comprises applying a fungicidally effective
amount of a mixture of an N-phenylcarbamate of the formula:

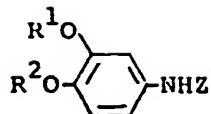


15 wherein R^1 , R^2 , R^3 , X, Y and Z are each as defined in claim
1 and a benzimidazole thiophanate fungicide and/or a cyclic
imide fungicide.

20 13. A process for producing an N-phenylcarbamate
of the formula:



25 wherein R^1 , R^2 , R^3 , X, Y, and Z are as defined in claim 1
which process comprises reacting a 3,4-dialkoxyaniline of
the formula:

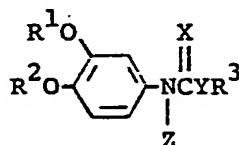


- wherein R^1 , R^2 and Z are each as defined in claim 1 with
 5 a chloroformate of the formula:

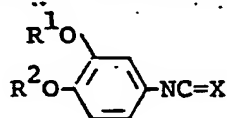


wherein R^3 , X and Y are each as defined in claim 1.

- 10 14. A process for producing an N-phenylcarbamate
 of the formula:



- 15 wherein Z is hydrogen and R^1 , R^2 , R^3 , X and Y are each as
 defined in claim 1, which process comprises reacting a 3,4-
 dialkoxyphenyl isocyanate or isothiocyanate of the formula:



- 20 wherein R^1 , R^2 and X are each as defined in claim 1 with an
 alcohol or thiol of the formula:

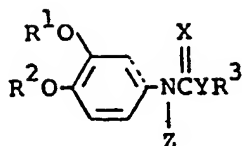


wherein R^3 and Y are each as defined in claim 1.

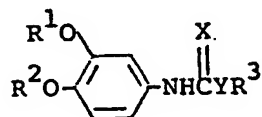
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15. A process for producing an N-phenylcarbamate
 of the formula:

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wherein Z is as defined in claim 1 but is other than hydrogen;
 5 and R¹, R², R³, X and Y are each as defined in claim 1, which
 comprises reacting a 3,4-dialkoxyphenylcarbamate of the
 formula:



10

wherein R¹, R², R³, X and Y are each as defined in claim 1
 with a halide of the formula:



wherein A is a halogen atom and Z is as defined in claim 1.

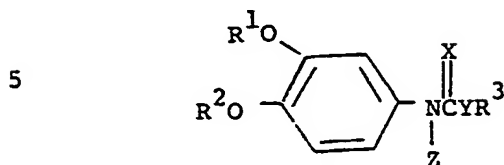
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CLAIMS FOR AUSTRIA

1. A process for producing an N-phenylcarbamate of the formula :



wherein R¹ and R² are the same or different and are each independently a lower alkyl group, a lower alkenyl group, a lower alkynyl group or a lower alkyl group substituted with at least one halogen atom, lower alkoxy or lower cycloalkyl group; R³ is a C₁-C₈ alkyl group, a C₃-C₈ alkenyl group, a C₃-C₈ alkynyl group, a lower cycloalkyl group, a lower haloalkenyl group, a lower haloalkynyl group, a lower aralkyl group, a lower alkyl group substituted with at least one halogen atom, cyano, lower alkoxy, lower alkenyloxy, lower haloalkoxy, phenoxy, lower aralkyloxy or lower cycloalkyl group,

or a group of the formula:

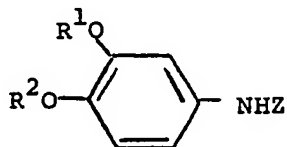
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in which m is 0, 1 or 2, n is 1, 2 or 3; X and Y are the same or different and each represent an oxygen atom or a sulfur atom; and Z is a hydrogen atom, a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a lower cycloalkyl group, a lower haloalkenyl group, a lower alkyl group substituted with at least one halogen atom, cyano, lower alkoxy or lower

- 2 -

alkoxycarbonyl group, or a group of the formula:

-COR⁴ or -SO₂R⁴ in which R⁴ is a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a lower cycloalkyl group, a lower haloalkenyl group, a lower alkyl group substituted with at least one halogen atom, cyano, lower alkoxy, lower cycloalkyl or phenoxy group (the phenoxy group optionally being substituted with at least one halogen atom and/or at least one alkyl group), a phenyl group, a furyl group, a thienyl group, a phenyl group substituted with at least one halogen atom, cyano, nitro, trifluoromethyl, lower alkyl or lower alkoxy group, or an aralkyl group (the aralkyl group optionally being substituted with at least one halogen atom and/or at least one alkyl group), with the proviso that when R¹ is methyl, R² is not methyl or butyl, which process comprises reacting a 3,4-dialkoxyaniline of the formula:

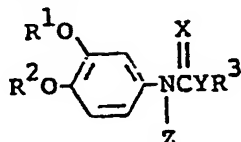


wherein R¹, R² and Z are each as defined above with a chloroformate of the formula:



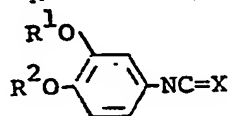
wherein R³, X and Y are each as defined in claim 1.

2. A process for producing an N-phenylcarbamate
of the formula:



5

wherein Z is hydrogen and R^1 , R^2 , R^3 , X and Y are each as defined in claim 1, which process comprises reacting a 3,4-dialkoxyphenyl isocyanate or isothiocyanate of the formula:



10

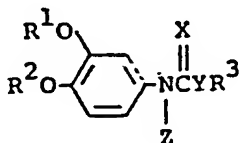
wherein R^1 , R^2 and X are each as defined in claim 1 with an alcohol or thiol of the formula:



15 wherein R^3 and Y are each as defined in claim 1.

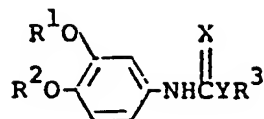
3. A process for producing an N-phenylcarbamate
of the formula:

20



wherein Z is as defined in claim 1 but is other than hydrogen and R^1 , R^2 , R^3 , X and Y are each as defined in claim 1, which
25 comprises reacting a 3,4-dialkoxyphenylcarbamate of the
formula:

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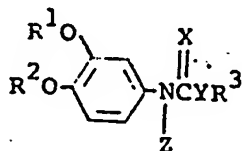


wherein R^1 , R^2 , R^3 , X and Y are each as defined in claim 1
 5 with a halide of the formula:



wherein A is a halogen atom and Z is as defined in claim 1.

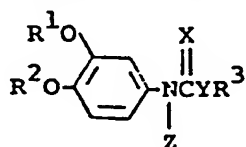
4. A method for controlling plant pathogenic
 10 fungi which comprises applying a fungicidally effective
 amount of at least one N-phenylcarbamates of the formula:



15 wherein R^1 , R^2 , R^3 , X, Y and Z are each as defined in claim
 1, to plant pathogenic fungi.

5. A method as claimed in claim 4 wherein the
 20 plant pathogenic fungi is the drug-resistant strain.

6. A method for controlling plant pathogenic
 fungi which comprises applying a fungicidally effective
 amount of a mixture of an N-phenylcarbamate of the formula:



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wherein R^1 , R^2 , R^3 , X, Y and Z are each as defined in claim 1 and a benzimidazole thiophanate fungicide and/or a cyclic imide fungicide.



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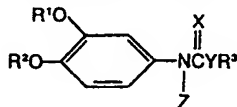
71 Applicant: **SUMITOMO CHEMICAL COMPANY, LIMITED,**
15 Kitahama 5-chome Higashi-ku, Osaka-shi Osaka-fu
(JP)

72 Inventor: **Noguchi, Hiroshi, 10-3-318,**
Sonehigashi-machi, 2-chome, Toyonaka Osaka (JP)
Inventor: **Kato, Toshiro, 8-D-410, Sakasedai, 1-chome,**
Takarazuka Hyogo (JP)
Inventor: **Takahashi, Junya, 4-2-303, Ryodo-cho,**
Nishinomiya Hyogo (JP)
Inventor: **Ishiguri, Yukio, 14-7, Mefu, 2-chome,**
Takarazuka Hyogo (JP)
Inventor: **Yamamoto, Shigeo, 2-16, Koda 2-chome, Ikeda**
Osaka (JP)
Inventor: **Kamoshita, Katsuzo, 3-11 Kofudai, 2-chome**
Toyono-cho, Toyono-gun Osaka (JP)

74 Representative: **Allard, Susan Joyce et al, BOULT,**
WADE & TENNANT 27 Farnival street, London EC4A 1PQ
(GB)

54 **Fungicidal N-phenylcarbamates.**

57 The use of an N-phenylcarbamate of the formula:



as a fungicidal agent against phytopathogenic fungi, particularly those strains which are resistant to benzimidazole thiophanate fungicides and/or cyclic imide fungicides.

EP 0 078 663 A3



European Patent
Office

EUROPEAN SEARCH REPORT

0078663
(Application Number)

EP 82 30 5714

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
A	CHEMICAL ABSTRACTS, vol. 28, no. 8, 20th April 1934, columns 2339,2340, Columbus, Ohio, USA BRUNNER et al.: "p-Methoxy- and 3,4-dimethoxyphenylurethans" & MONATSH., 63, 374-84, 1933 -----	1	C 07 C 125/065 C 07 C 143/83 C 07 C 155/00 C 07 D 307/20 C 07 D 307/42 A 01 N 47/10
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
			C 07 C 125/00 C 07 C 155/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 06-04-1983	Examiner GAUTIER R.H.A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	